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Reduction of Defects in Germanium-Silicon

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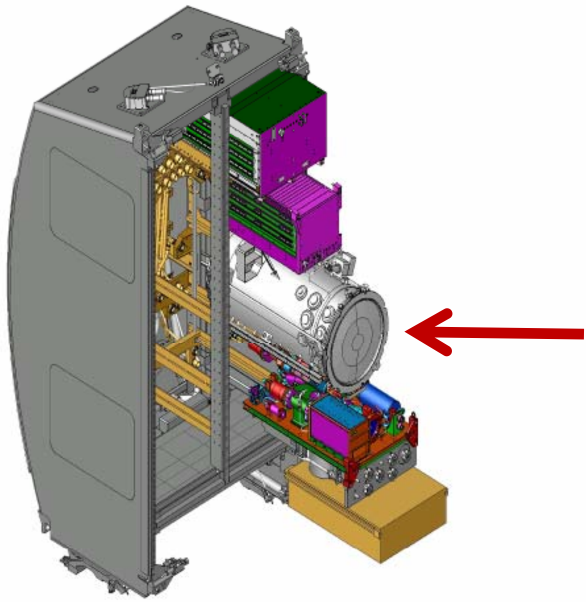
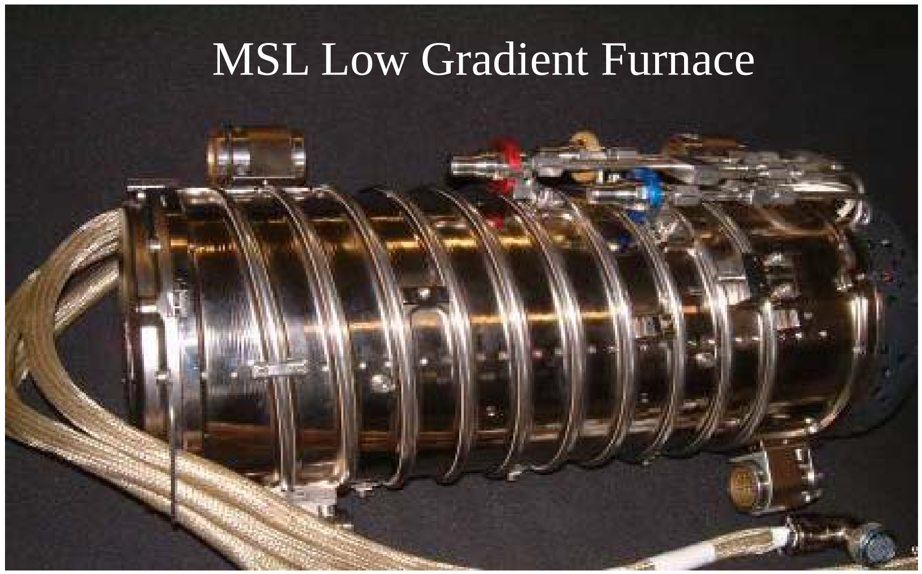
RDGS Flight Investigation

- "Reduction of Defects in Germanium-Silicon" (RDGS) is a NASA Materials Science Flight Investigation
- RDGS is a collaborative investigation between NASA and the European Space Agency (ESA)
- The RDGS experiments will be conducted in the Low Gradient Furnace (LGF) in the Materials Science Laboratory on the International Space Station (ISS)



Materials Science Laboratory

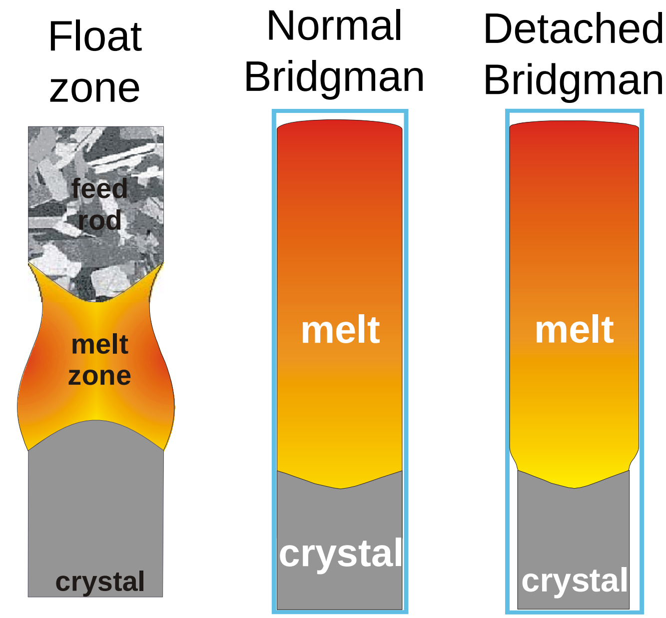


MSL Low Gradient Furnace

Overview of Investigation

This investigation involves the comparison of results achieved from three types of crystal growth of germanium and germanium-silicon alloys:

- Float zone growth
- Bridgman growth
- Detached Bridgman growth



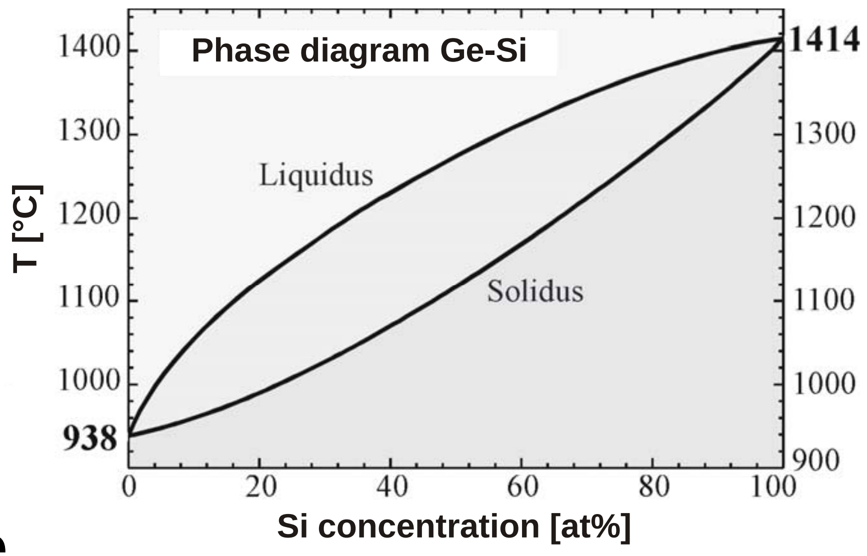
An understanding of the de-wetting process that enables detached Bridgman growth and of the roles of thermo- and solutocapillary convection in determining the characteristics of float zone Ge-Si crystals are the prerequisite objectives of this investigation. The fundamental objective is a quantitative comparison of the defects induced by various growth factors among the three types of growth methods.

Why Study Germanium-Silicon Alloys?

- Technological applications
  - X-ray and neutron optics (gradient crystals)
  - High-efficiency solar cell material
  - Thermoelectric converters
  - High-speed, high frequency electronic devices (HBTs, HBFETs) as alternative to GaAs
- Characterization methods for silicon and germanium are well-established and are applicable to the alloy crystals.
- Relatively well known material properties and material parameters
- The vapor pressure of silicon and germanium melts can be neglected; they are non-toxic materials.

Technological Challenges of $Ge_{1-x}Si_x$

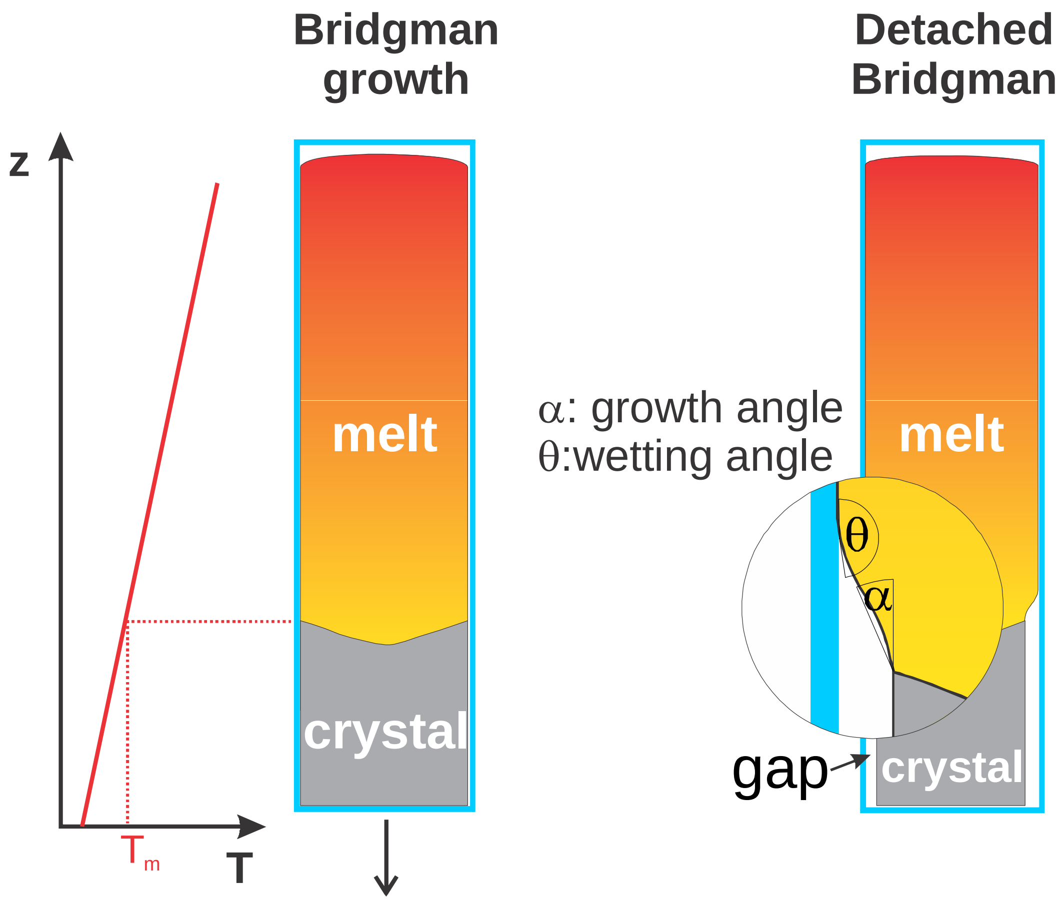
- Large separation of solidus and liquidus curves leads to strong segregation
- Lattice mismatch (4%) leads to increased stress, cracks, high dislocation densities, polycrystalline growth
- The reactivity of liquid silicon leads to a reaction with crucible materials (sticking) as well as contamination of the melt and the crystals



Principles of Detached Bridgman Growth

Sufficient condition for detachment[1,2]:

$$(\alpha+\theta \geq 180°)$$



Advantages

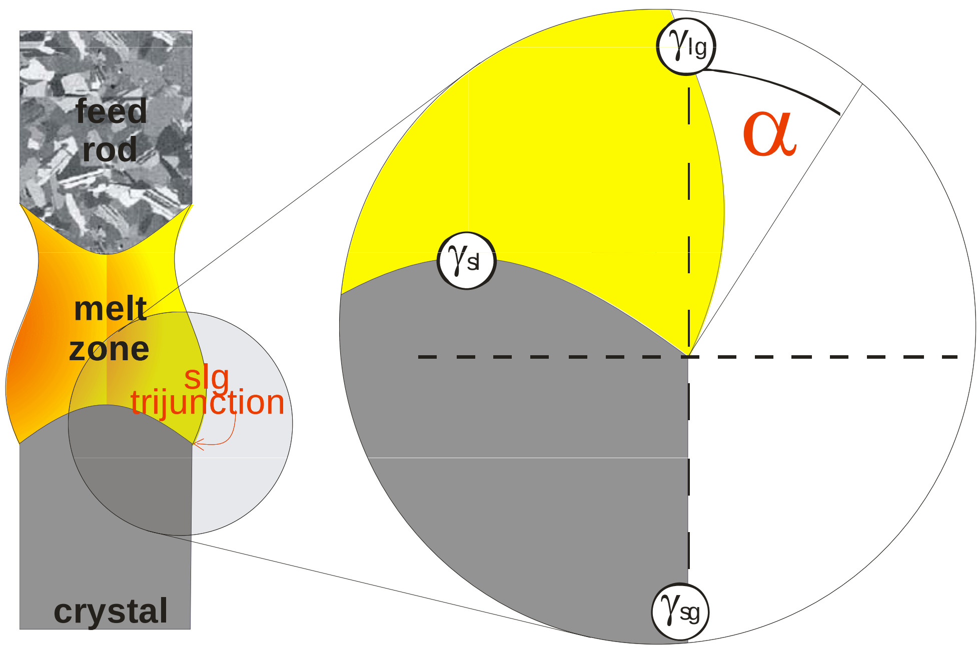
- No sticking of the crystal to the ampoule wall
- Reduced stress
- Reduced dislocations
- No heterogeneous nucleation by the ampoule
- Reduced contamination

[1]V. S. Zemskov: Fiz. Khim. Obrab. Mater. 17 (1983) 56

[2]T.Duffar, I.Paret-Harter, P.Dusserre: J.Crystal Growth 100 (1990) 171.

Growth Angle and Wetting Angle

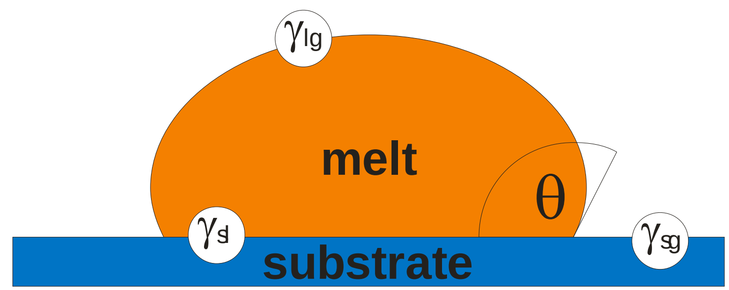
Growth angle α:



$$\alpha = \arccos\left(\frac{\gamma_{sg}^2 + \gamma_{lg}^2 - \gamma_{sl}^2}{2 \cdot \gamma_{sg} \cdot \gamma_{lg}}\right)$$

W.Bardsley, F.C. Frank, G.W. Green, D.T.J. Hurle: J. Crystal Growth 23 (1974), 341

Wetting angle θ:



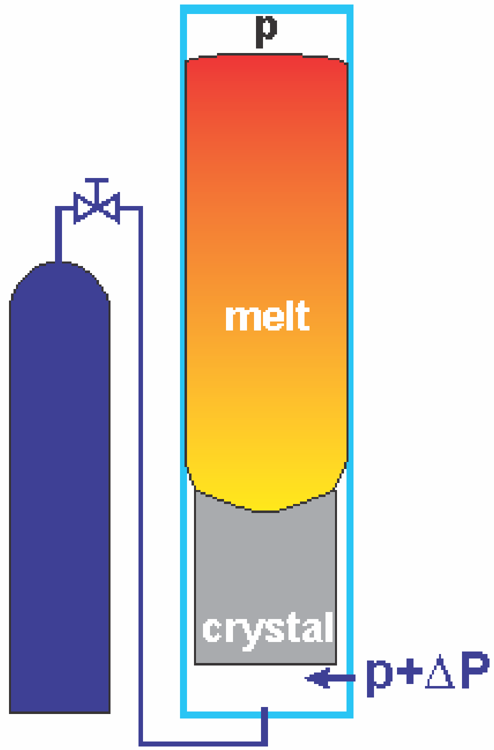
$$\theta = \arccos\frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

(Young equation)

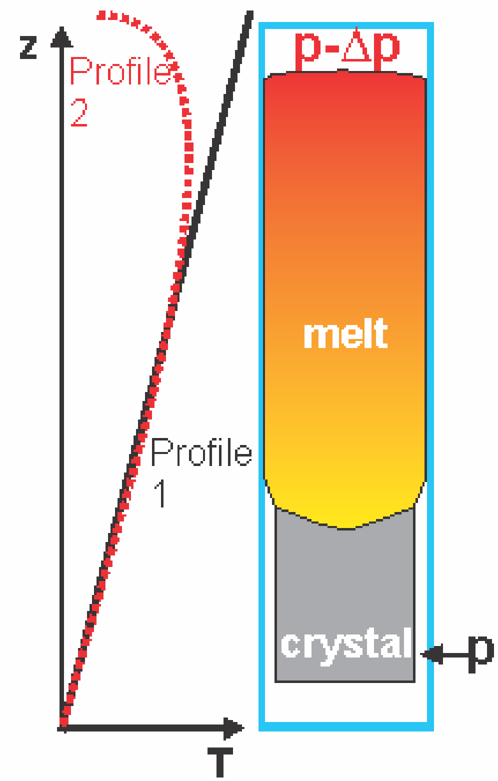
γ_{lg}: surface energy liquid-gas
γ_{sl}: surface energy solid-liquid
γ_{sg}: surface energy solid-gas

Gas Pressure Below Meniscus

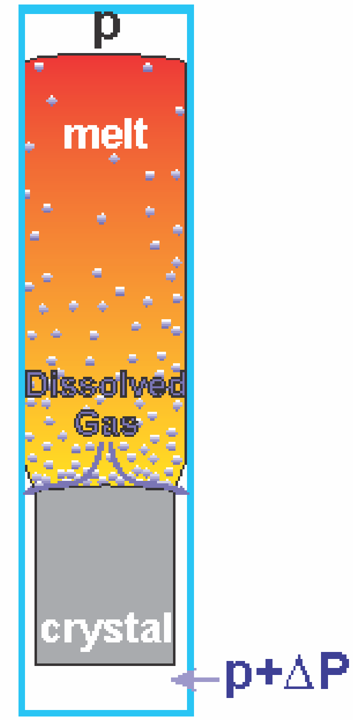
Higher pressure below the meniscus by active pressurization



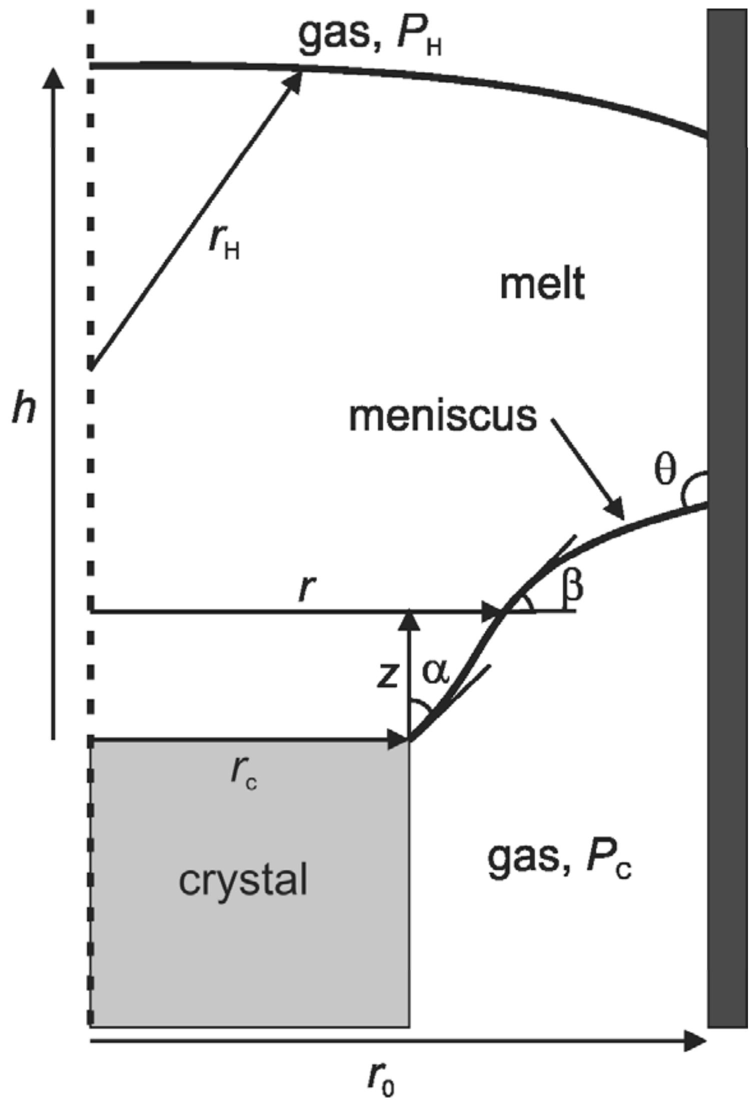
Higher pressure below the meniscus by temperature reduction above the melt



Higher pressure below the meniscus due to segregation at the interface



Schematic Diagram of Detached Solidification



M. P. Volz, K. Mazuruk, *Journal of Crystal Growth* 321 (2011) 29-35

Calculation of Meniscus Shapes

$$\frac{\dfrac{d^2z}{dr^2}}{\left(1+\left(\dfrac{dz}{dr}\right)^2\right)^{3/2}}+\frac{\dfrac{dz}{dr}}{r\left(1+\left(\dfrac{dz}{dr}\right)^2\right)^{1/2}}=\Delta P-Bz(r)$$

Young-Laplace Equation

$$\Delta P=\frac{\Delta P_m r_0}{\sigma},\quad \Delta P_m=P_H-P_C+\rho gh+2\frac{\sigma}{r_H}$$

ΔP : Dimensionless pressure differential across the meniscus

$$B=\frac{\rho g_0 r_0^{\,2}}{\sigma}$$

B = 3.248; Ge, r_0 = 6 mm
B = 4.651; InSb, r_0 = 5.5 mm

B : Bond number; ratio of gravity force to surface tension force

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$$\frac{\partial r}{\partial s}=\cos\beta,\quad \frac{\partial z}{\partial s}=\sin\beta,\quad \frac{\partial\beta}{\partial s}=-\frac{\sin\beta}{r}+\Delta P-Bz$$

Set of 3 coupled differential equations

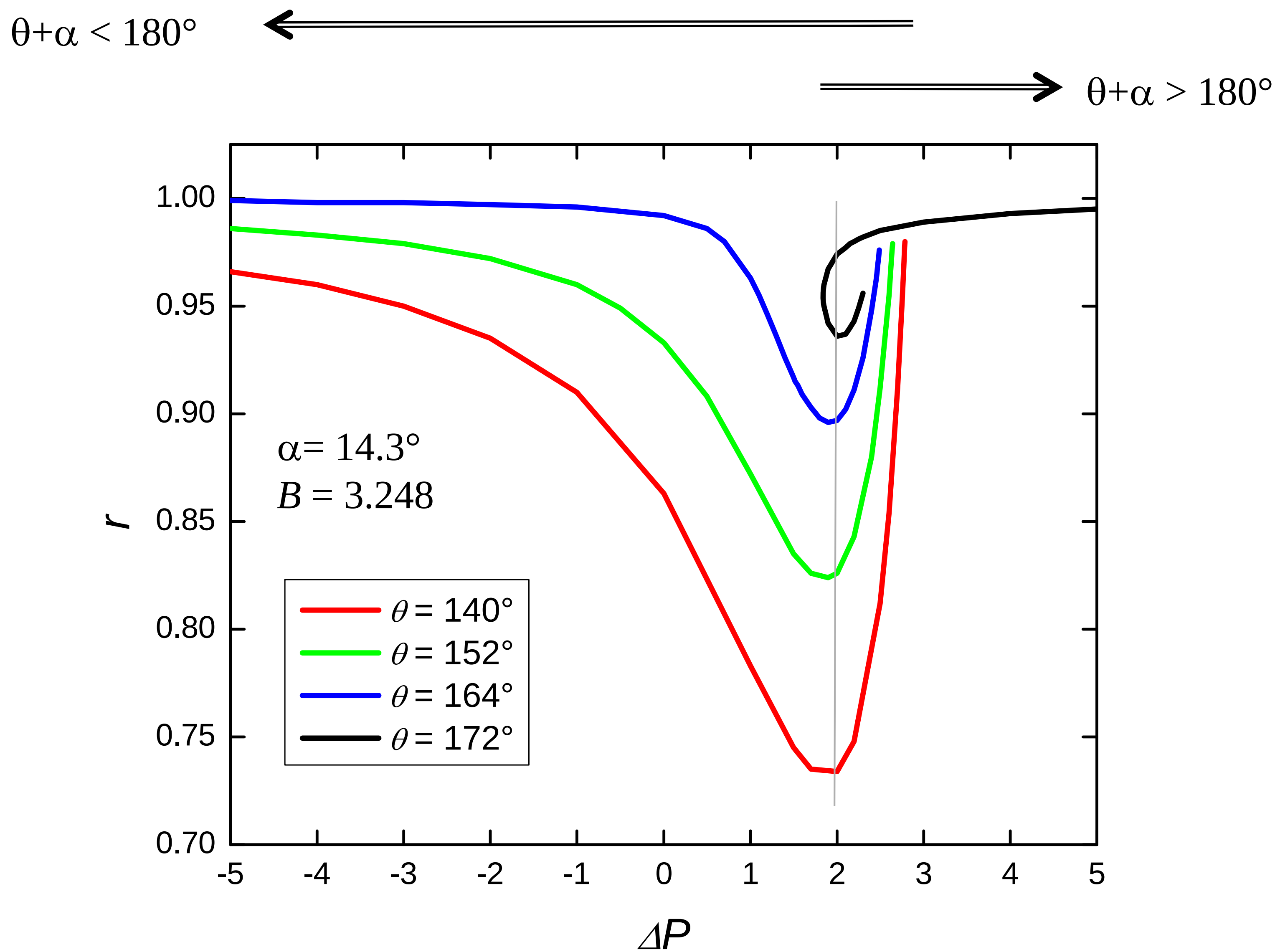
Boundary Conditions

$z(0) = 0$; $\beta(0) = 90° - \alpha$;

$\beta(1) = \theta - 90°$; $r(1) = 1$

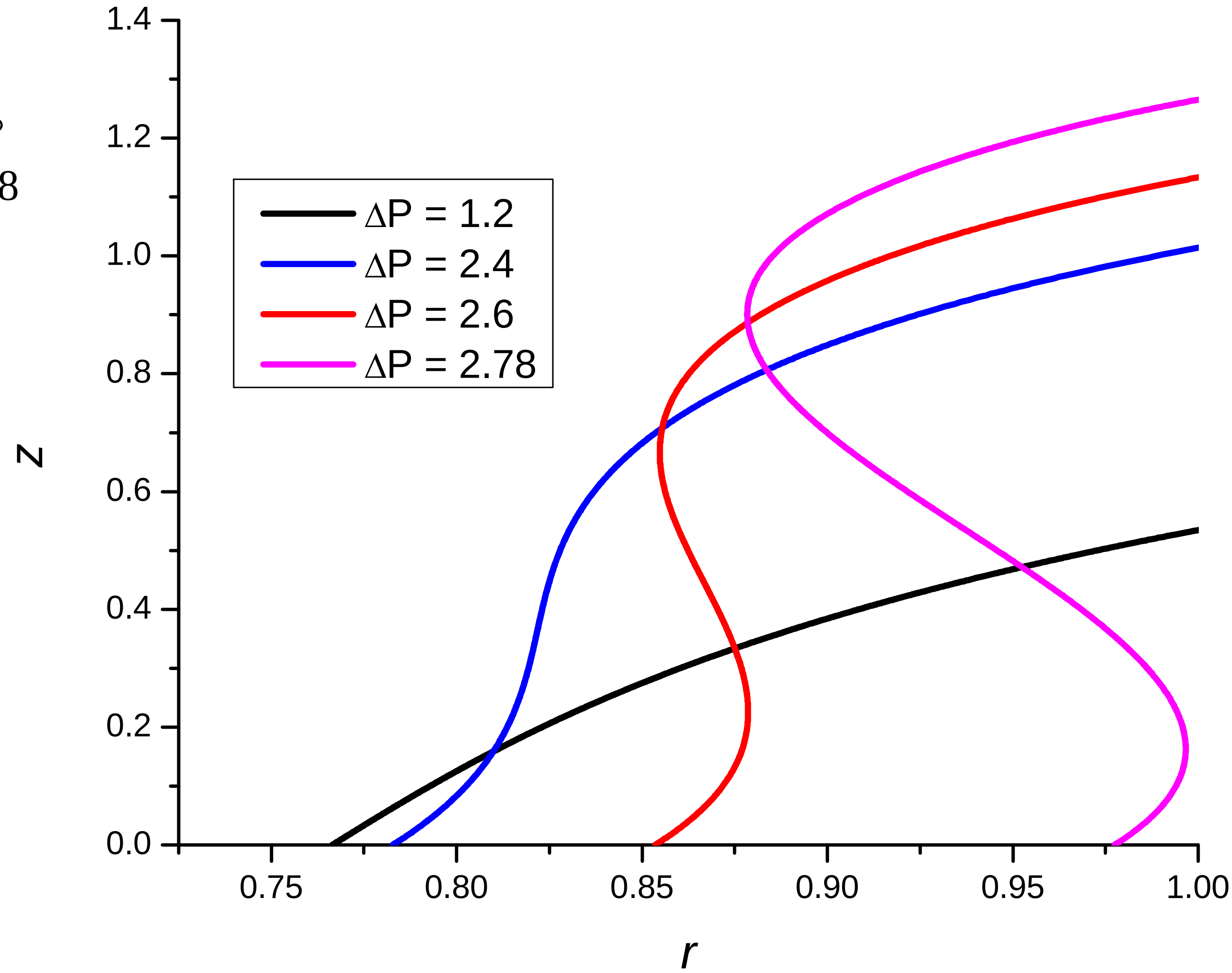
α: growth angle
θ: contact or wetting angle

Gap Width vs. Pressure Differential (Ge at 1*g*)

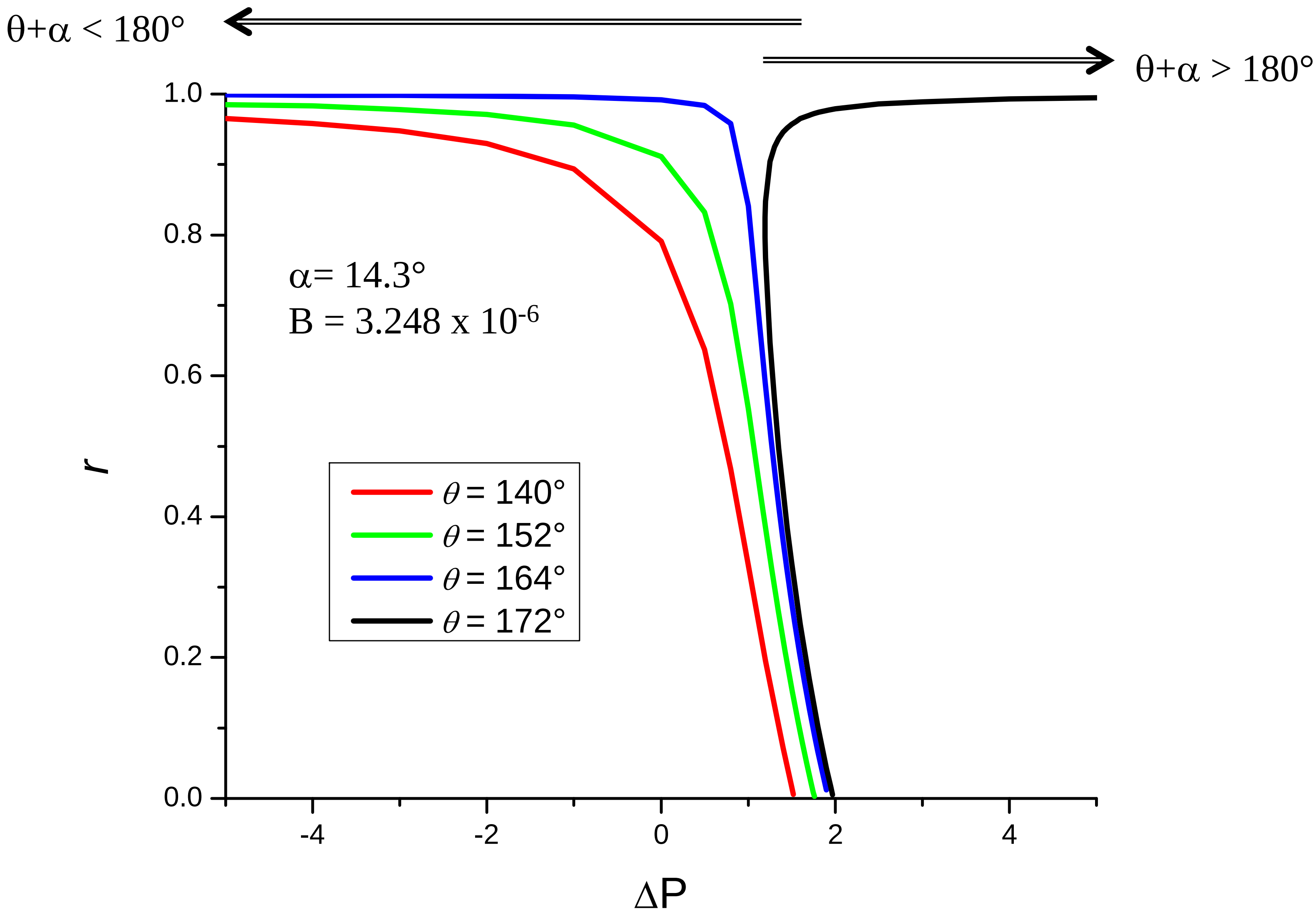


Meniscus Shapes vs. ΔP for $\theta = 140°$

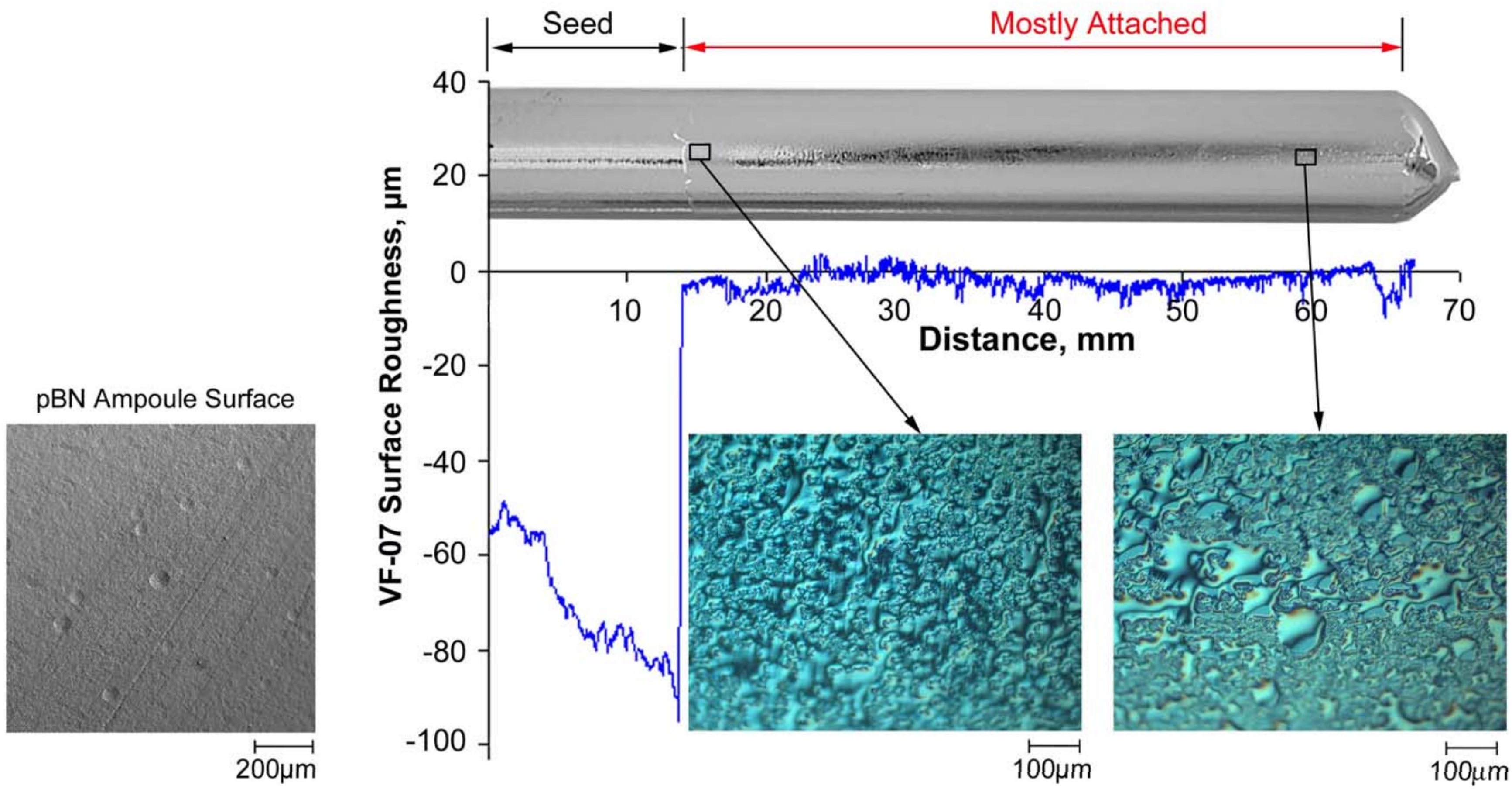
$\alpha = 14.3°$
$B = 3.248$



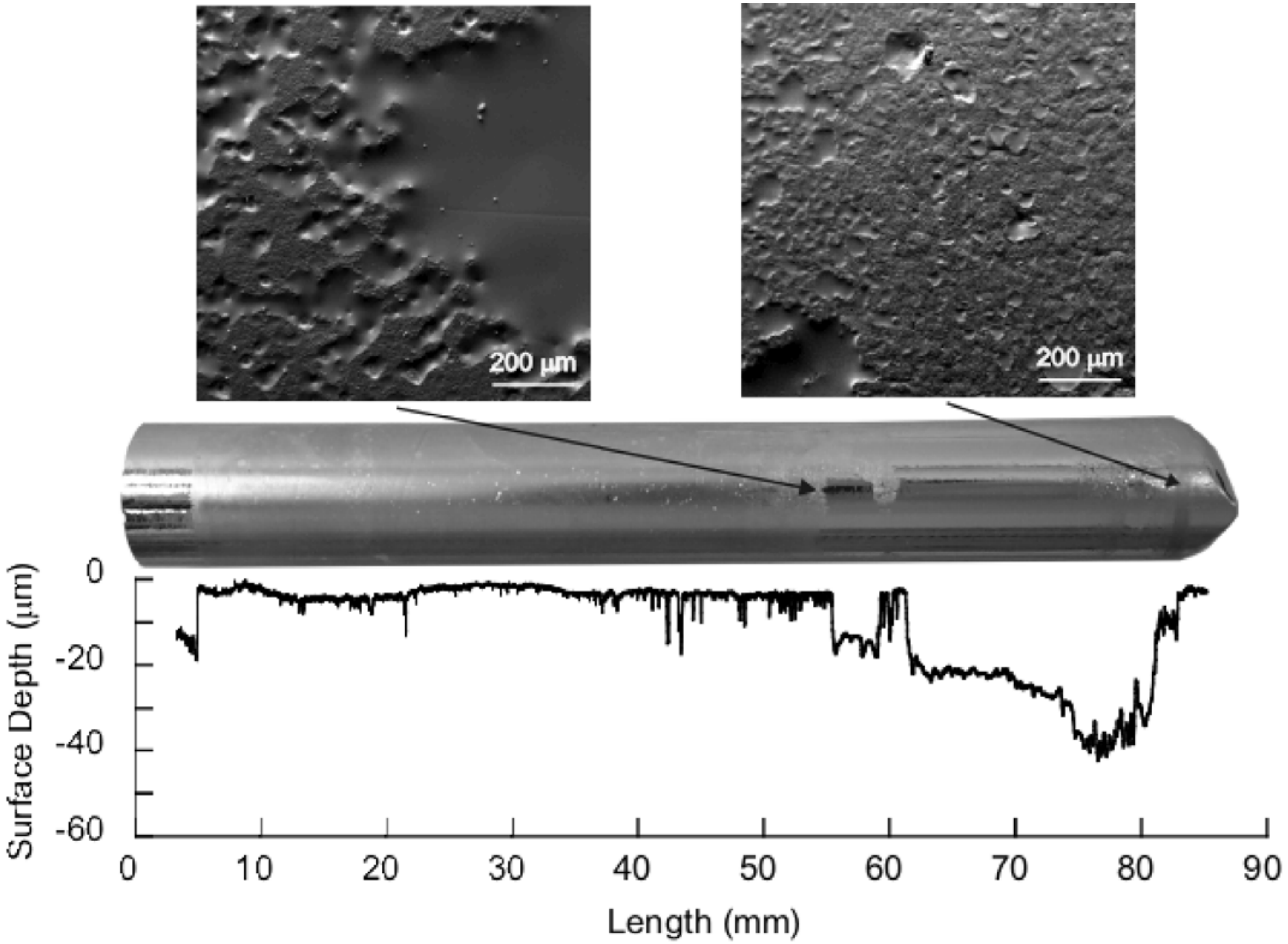
Gap Width vs. Pressure Differential (Ge at $g = 1 \times 10^{-6}\ g_0$)



“Attached” Germanium

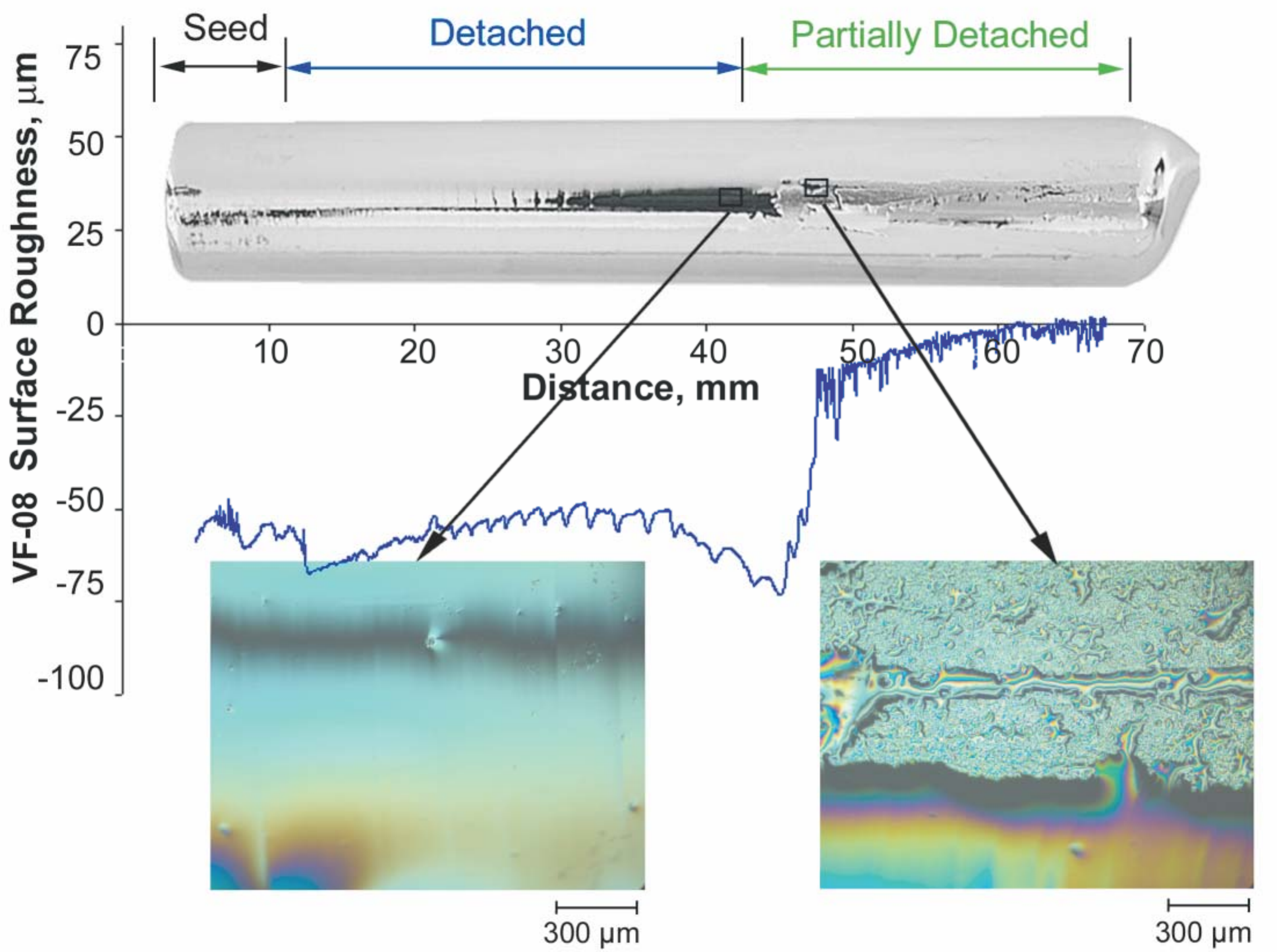


Partially Attached GeSi



M. P. Volz, M. Schweizer, N. Kaiser, S. D. Cobb, L. Vujisic, S. Motakef, F. R. Szofran, *JCG* 237-239 (2002) 1844-1848

Detached Ge in pBN Ampoule



In-situ Pressure Control Setup

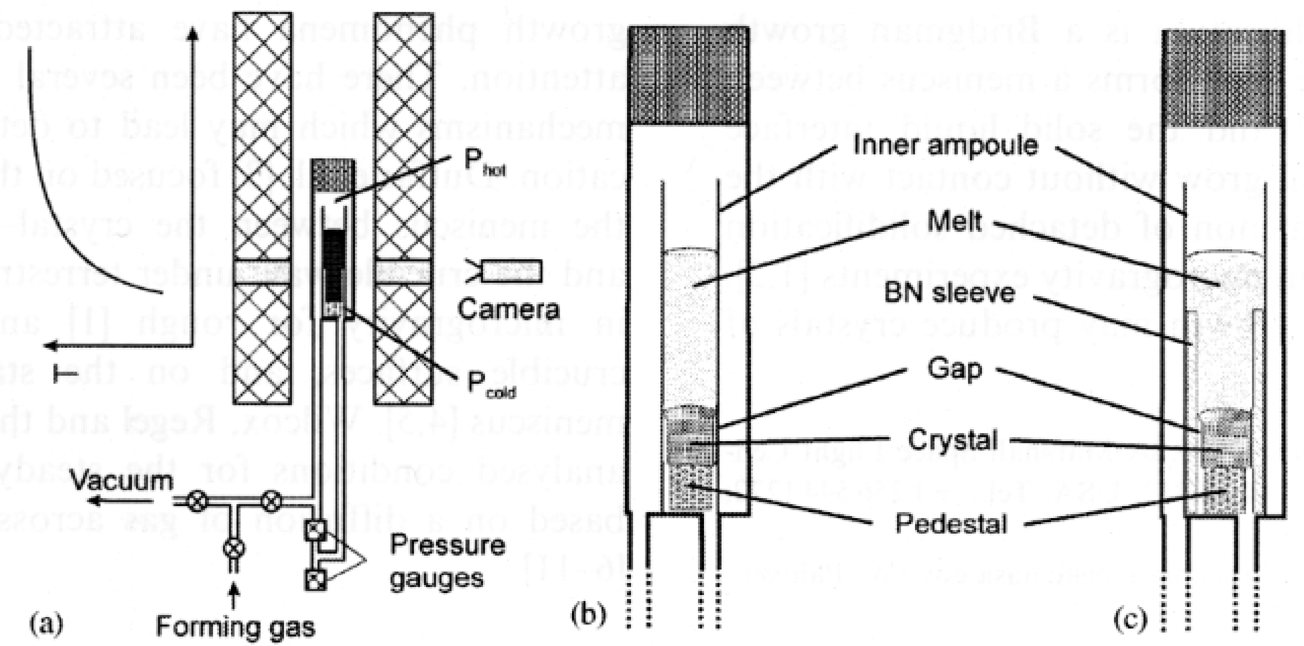
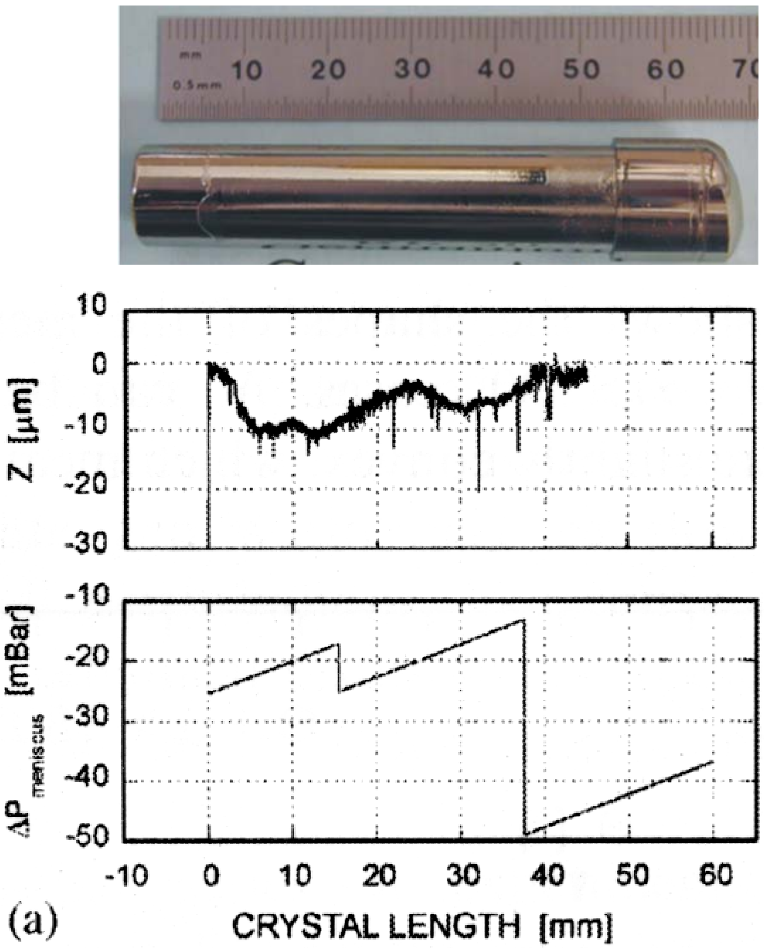
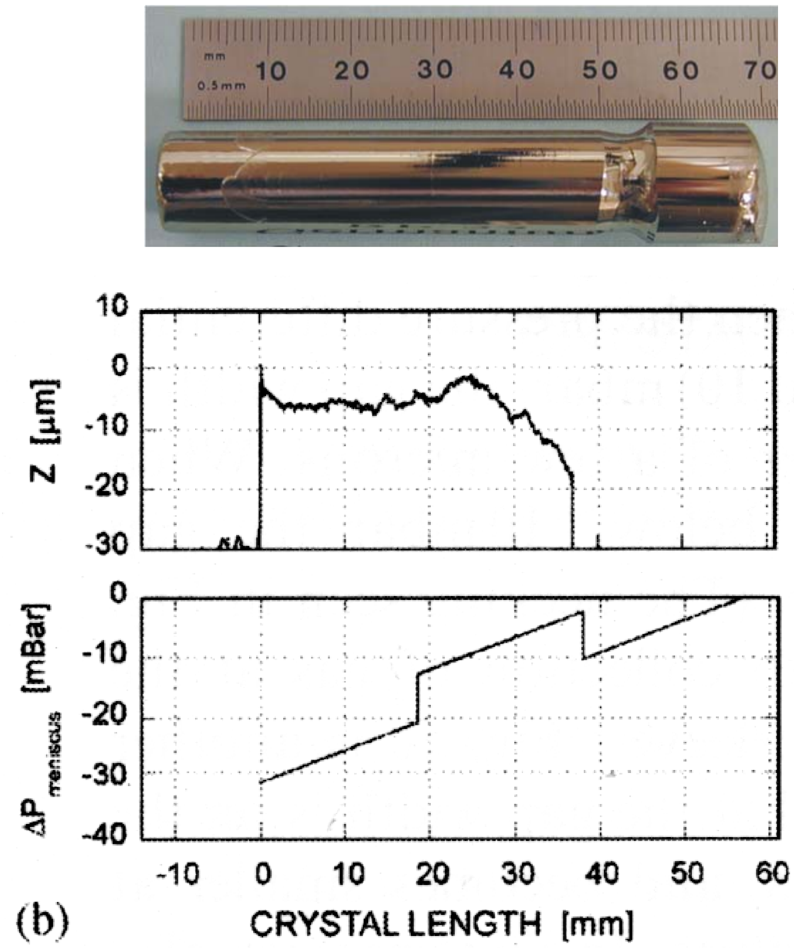


Fig. 1. Experimental system: (a) growth configuration; (b) ampoule with silica crucible; (c) ampoule with pBN insert.

W. Palosz, M. P. Volz, S. Cobb, S. Motakef, F. R. Szofran, *JCG* 277 (2005) 124-132

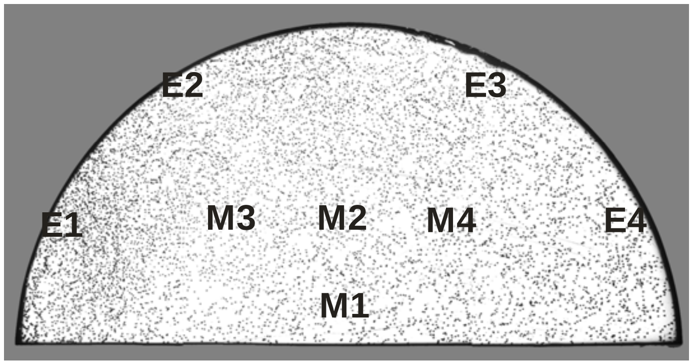
Ge Grown with Controlled ΔP





W. Palosz, M. P. Volz, S. Cobb, S. Motakef, F. R. Szofran, *JCG* 277 (2005) 124-132

Propagation of Defects in Detached/Attached Crystals



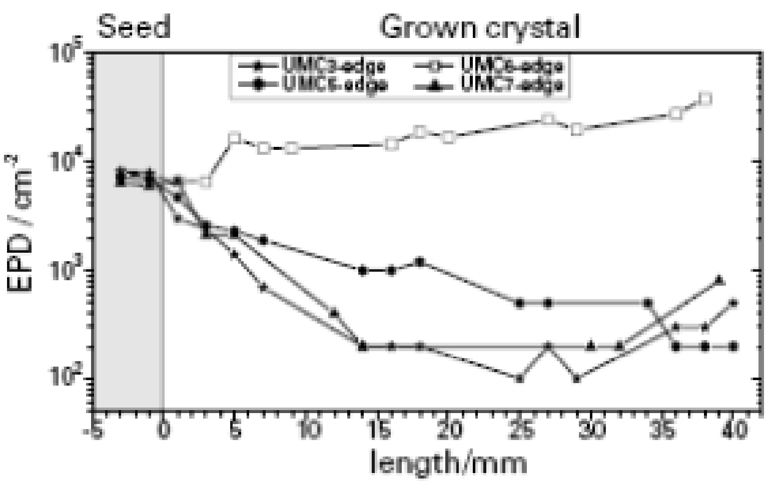


Fig. 3. Axial EPD variation along the edge in detached- (closed symbols) and attached-grown (open symbols) crystals. In the detached-grown crystals the EPD is reduced more than two orders of magnitude compared to the attached-grown crystal UMC6.

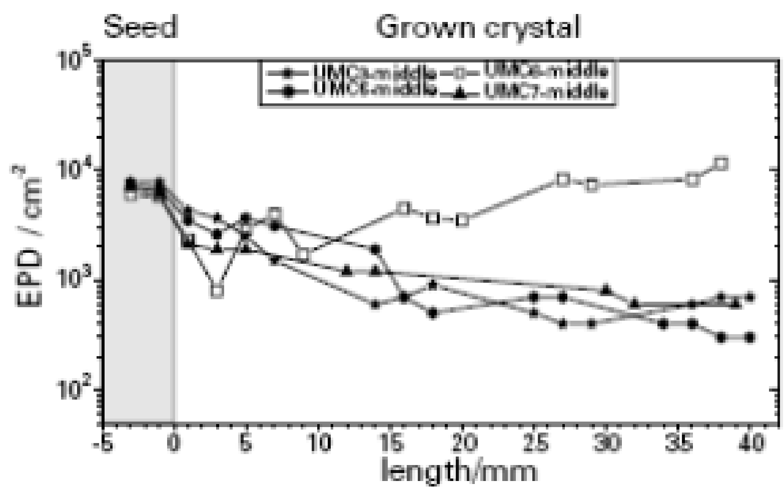


Fig. 4. Axial EPD variation in the middle in detached- (closed symbols) and attached-grown (open symbols) crystals.

M. Schweizer, S. D. Cobb, M. P. Volz, J. Szoke, F. R. Szofran, *JCG* 235 (2002) 161-166

Etch Pit Densities in Detached/Attached Crystals

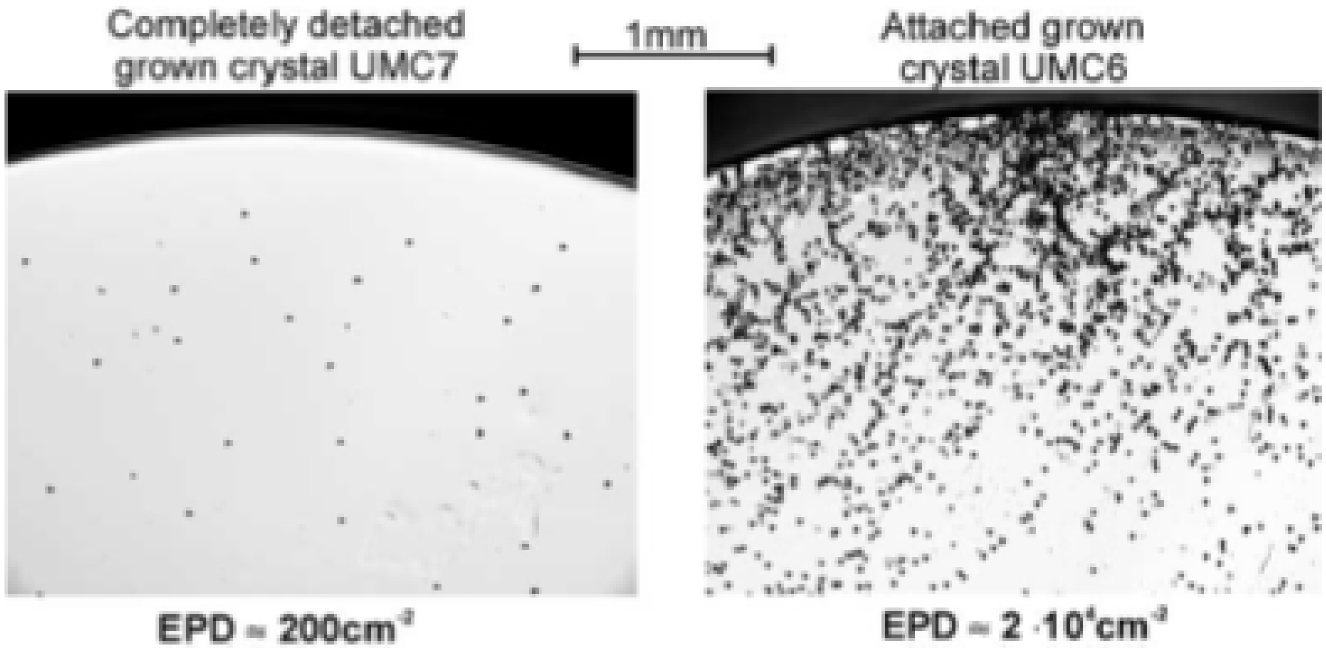


Fig. 5. Micrograph from the detached-grown sample UMC7 and from the attached-grown sample UMC6.

M. Schweizer, S. D. Cobb, M. P. Volz, J. Szoke, F. R. Szofran, *JCG* 235 (2002) 161-166

Etch Pit Density Variation With Attachment

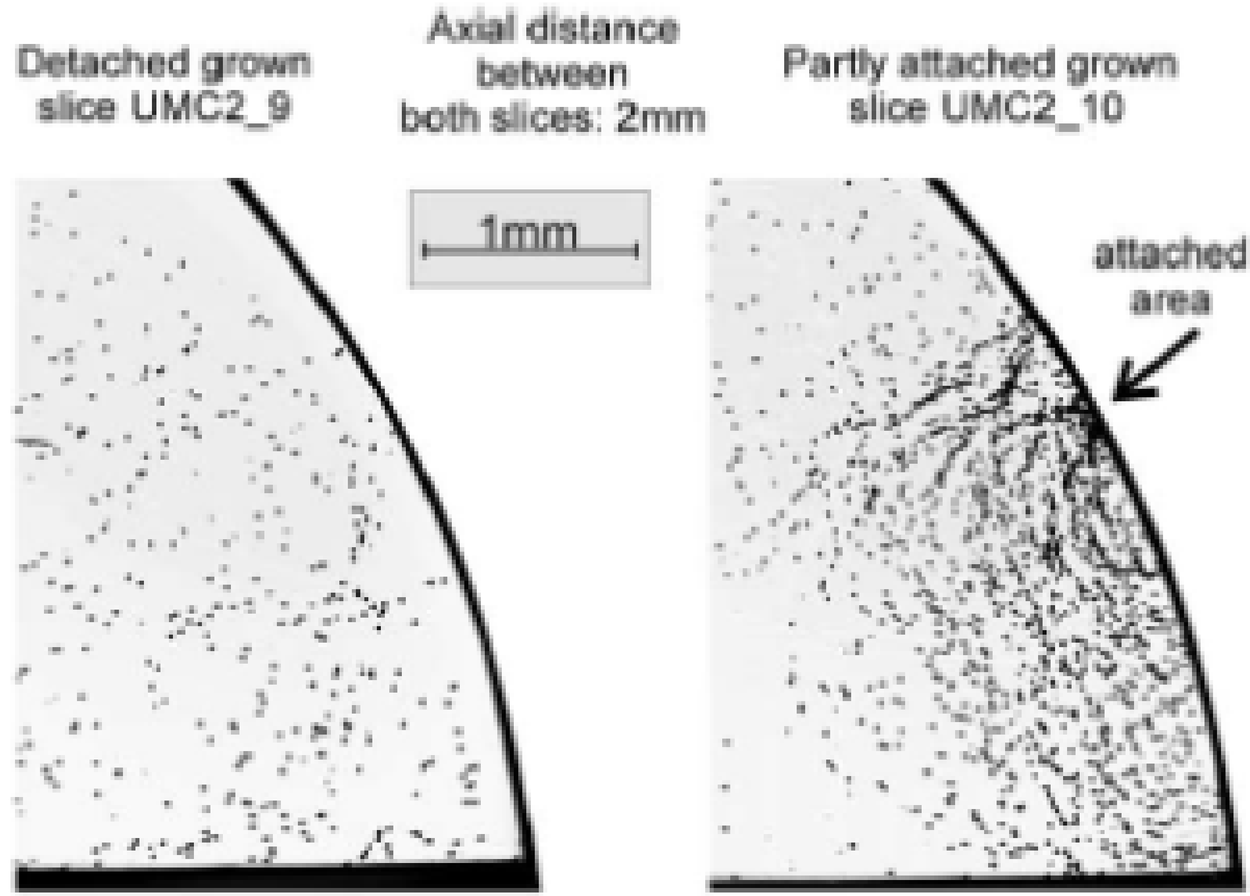
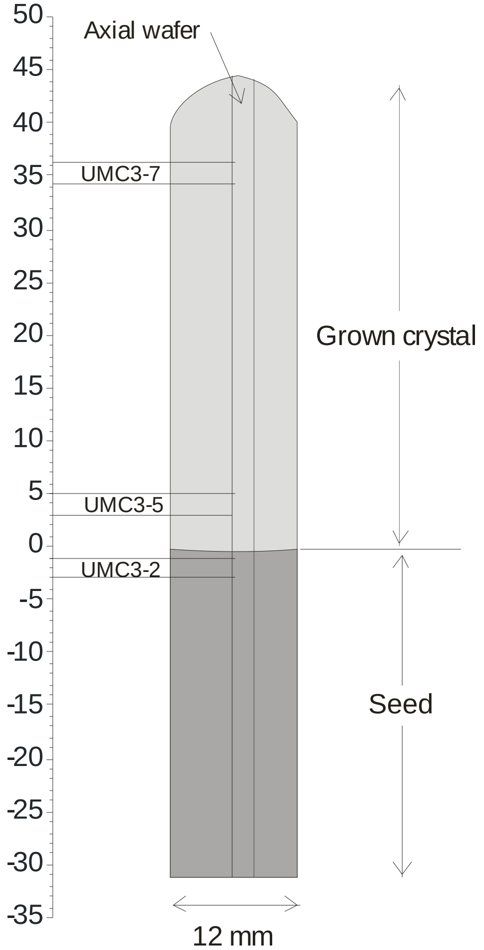


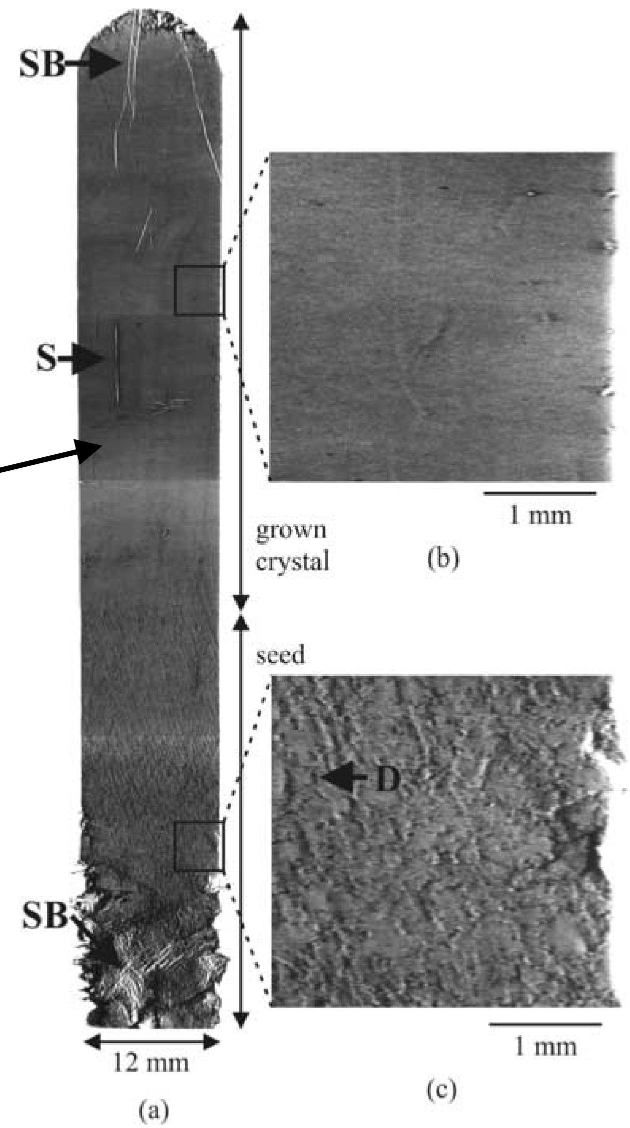
Fig. 6. Localized increased EPD after the crystal attaches partially to the wall.

M. Schweizer, S. D. Cobb, M. P. Volz, J. Szoke, F. R. Szofran, *JCG* 235 (2002) 161-166

X-Ray Synchrotron Topography of Detached Ge

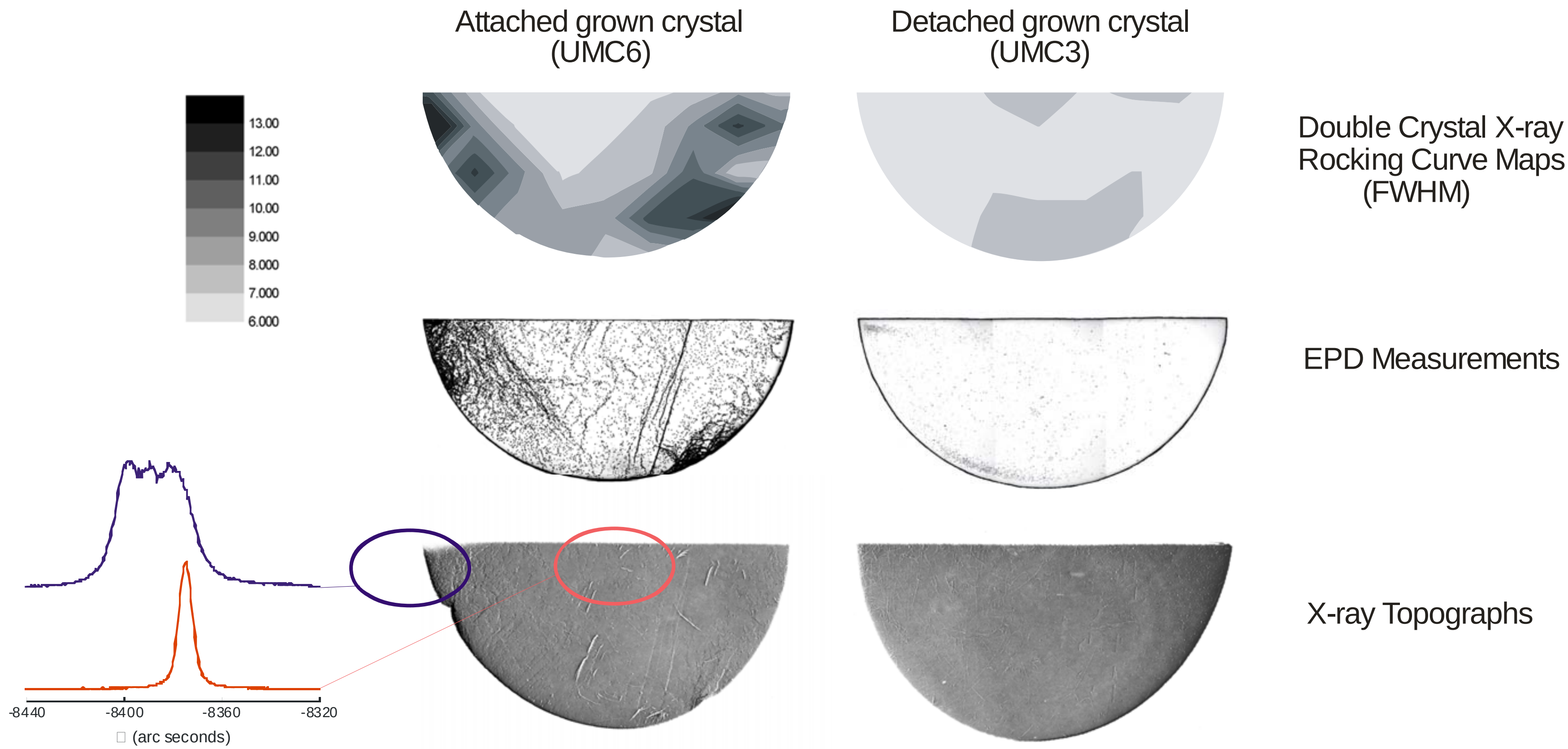


220 reflection topograph (l = 0.69 Å) recorded from a detached-grown UMC3 crystal wafer cut parallel to the growth axis (S – scratch, SB – subgrain boundary, D – dislocation).



M. P. Volz, M. Schweizer, B. Raghothamachar, M. Dudley, J. Szoke, S. D. Cobb, F. R. Szofran, JCG 290 (2006) 446-451

Double Crystal Rocking Curve Maps of Detached Ge



M. P. Volz, M. Schweizer, B. Raghothamachar, M. Dudley, J. Szoke, S. D. Cobb, F. R. Szofran, *JCG* 290 (2006) 446-451

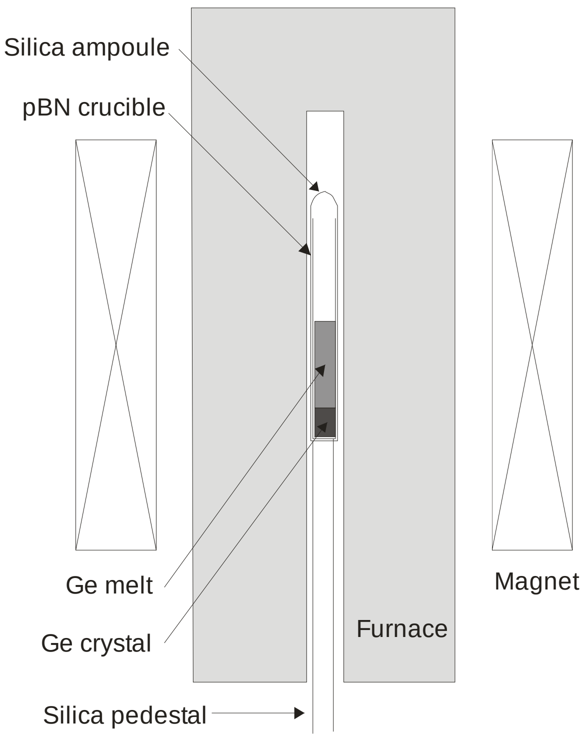
Rotating Magnetic Fields for $Ge_{1-x}Si_x$ Growth

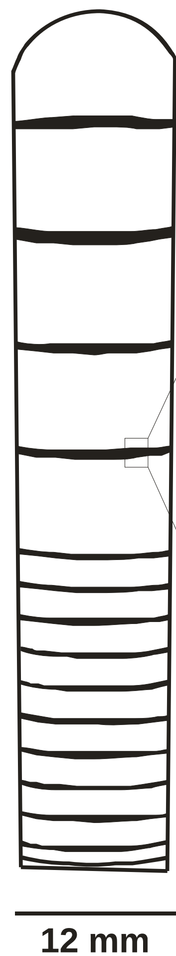
A rotating magnetic field is available on the LGF furnace and is expected to be utilized for the RDGS experiments. There are several potential uses for the RMF which include the following:

- Mix GeSi alloys prior to growth
- Affect (flatten) the melt/crystal interface shape
- Intentionally cause periods of flow instability or demarcations in the crystals
- Suppress thermal or solutal convection
- Affect the transport of dissolved gas from the melt/crystal interface

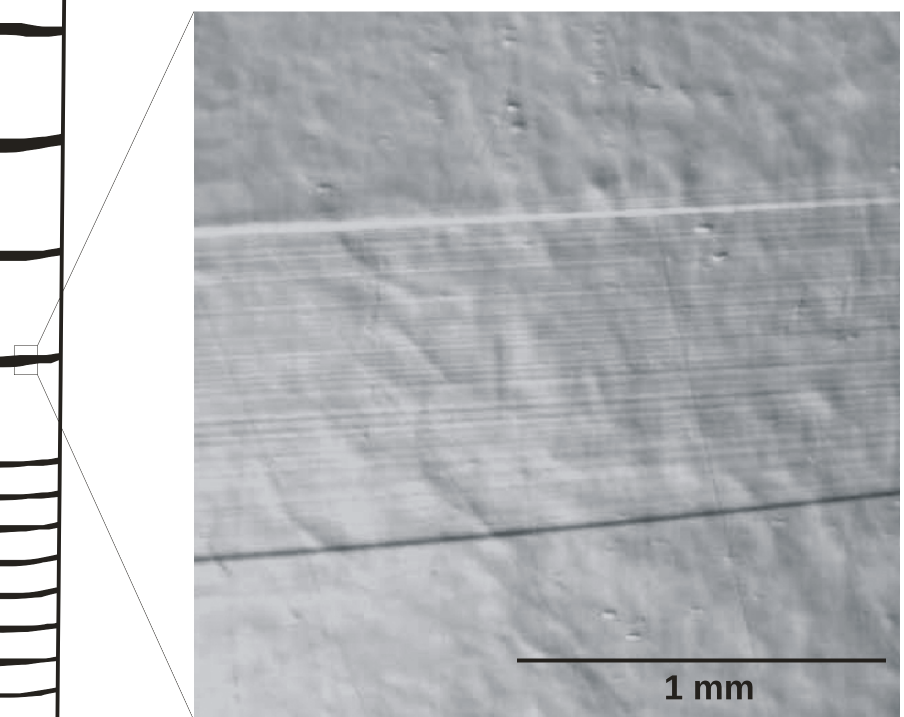
  - Calculations suggest that RMF produces radially inward flow at the melt /crystal interface, so that rejected gas is convected away form the detached free surface (J. S. Walker, M. P. Volz, F. R. Szofran, S. Motakef, *J. Mat. Synth. Proc.* 9, (2001) 73-81)

Bridgman Growth in a Rotating Magnetic Field





RMF Pulse



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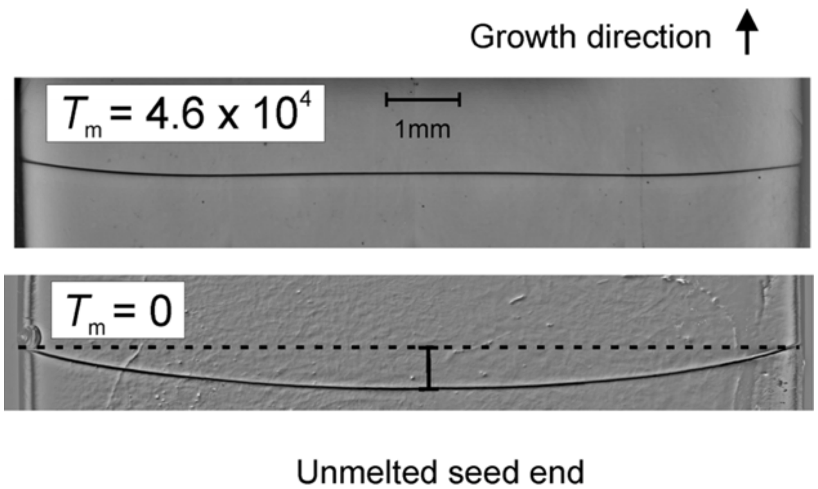
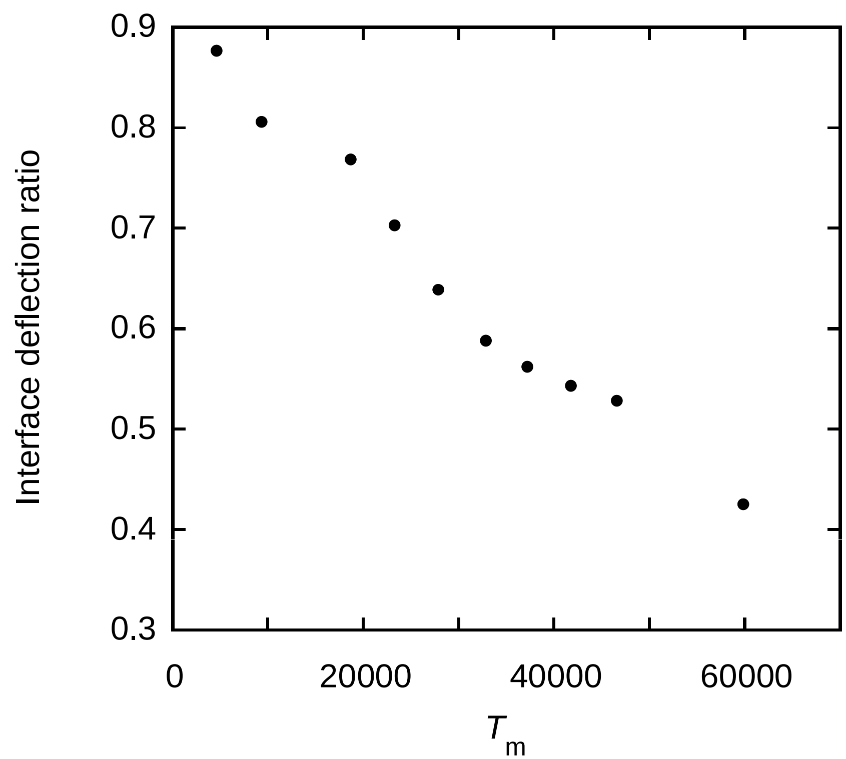
Effect of RMF on Interface Shape



Influence of a RMF on the growth interface shape. The RMF decreases the concavity and induces a w-shape.



Ratio of the interface deflection with a RMF on to the interface deflection with a RMF off.

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Flight Experiment Objectives

1. Determine the influence of containment on processing defects and impurity incorporation in germanium-silicon crystals.
2. Test the theory of detachment by evaluating the following parameters: pressure difference across the meniscus, growth angle, contact angle, and Bond number (ratio of gravitational and capillary forces).
3. Determine the influence of thermo- and solutocapillary convection along the free melt at the meniscus on the compositional segregation.
4. Control time-dependent STDC (Surface Tension Driven Convection) by the use of rotating magnetic fields. Examine the influence of the RMF on the heat and mass transport and the interface curvature.
5. Quantitatively compare the defect structure and impurity levels of microgravity-grown normal and detached Bridgman and float-zone crystals to determine the optimum growth process.

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